PATENT ABSTRACTS OF JAPAN

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(54) SHARK CARTILAGE EXTRACT AND METHOD FOR PRODUCING THE SAME

(57)Abstract:
PROBLEM TO BE SOLVED: To obtain a shark cartilage extract having low arsenic content and no nasty taste and smell and suitable for food materials, and to provide a method for producing the extract.
SOLUTION: The method for producing the shark cartilage extract having low arsenic content and no nasty taste and smell comprises extracting a shark cartilage extracted solution from shark cartilage raw material previously washed in water, decoloring and deodorizing the resultant shark cartilage extracted solution as it is or after being enzymically hydrolyzed, and subjecting the resultant decolored and deodorized shark cartilage extracted solution or its enzymically hydrolyzed solution to a separation film treatment.

LEGAL STATUS

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CLAIMS

[Claim(s)]
[Claim 1] the shark washed with water beforehand -- the shark obtained by carrying out demarcation membrane processing of the extract extracted from the cartilage raw material -- the shark characterized by being a cartilage extract and an arsenic content being 5 ppm or less -- a cartilage extract.
[Claim 2] a shark -- the process which washes a cartilage raw material with water, and said shark which washed -- the shark from a cartilage raw material -- the shark obtained at the process which extracts a cartilage extract, and said process -- the shark which was obtained in a cartilage extract at remaining as it is or the process which decolorizes and deodorizes, and said process after understanding by the enzyme and which decolorized and deodorized -- the shark characterized by to include the process which carries out the demarcation membrane processing of a cartilage extract or its zymolysis liquid -- the manufacture approach of a cartilage extract.
[Claim 3] said washed shark -- the shark from a cartilage raw material -- the extract of a cartilage extract -- said washed shark -- the shark according to claim 2 performed by adding water to a cartilage raw material and carrying out application-of-pressure heating -- the manufacture approach of a cartilage extract.
[Claim 4] said shark -- decolorization of a cartilage extract or its zymolysis liquid, and deordorization -- said shark -- the shark according to claim 2 or 3 performed by contacting a cartilage extract or its zymolysis liquid to a solid adsorbent -- the manufacture approach of a cartilage extract.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] the shark which this invention has few arsenic contents, and does not have a different taste and a nasty smell -- it is related with a cartilage extract and its manufacture approach.
[0002]
[Description of the Prior Art] a shark -- the cartilage extract is widely used as a health food raw material, and the major component is sodium chondroitin sulfate which is about several 100,000 polysaccharide from molecular weight 100,000. Since chondroitin sulfate is widely distributed also over the body and that on the cartilage and the skin of the joint section is especially contained in it, it is used for the health food aiming at an improvement and cosmetics of the osteoarthritis. [many]
[0003] the shark marketed now -- a sodium-chondroitin-sulfate content is 10 - 40%, and the cartilage extract is properly used with the purpose of use and price. Moreover, although the sodium chondroitin sulfate (about 85% or more) which raised whenever [purification] is used as a drugs raw material, it is expensive and it is hard to use it in the food field.
[0004] the former and a shark -- a cartilage extract -- sharks, such as a fillet of a shark, -- after contacting the extract obtained from the cartilage raw material by the approach of carrying out decomposition clearance of the protein which is extracted with lye or neutral salt liquid, and which adds a proteolytic enzyme and lives together etc. to a solid adsorbent and decolorizing and deodorizing, it is manufactured by carrying out spray drying etc.
[0005]
[Problem(s) to be Solved by the Invention] however, a shark -- many arsenics are contained in the cartilage raw material compared with other raw materials, such as a cow and a cartilage of a salmon, it will be condensed in an extract and a purification process (the conventional shark arsenic content of a cartilage extract : 40-50 ppm), and worth of goods was reduced remarkably.
[0006] furthermore, a shark -- the characteristic low-grade amine etc. existed in the cartilage raw material, just the deordorization processing by the above solid adsorbents of clearance of this nasty smell component is inadequate, and the nasty smell remained in the final product.
[0007] Moreover, clearance of the peptide which presents the bitterness generated with a proteolytic enzyme is difficult for the above-mentioned enzymatic process, and it had had the adverse effect on quality.
[0008] The approach of settling a mucopolysaccharide with alcohol and on the other hand, collecting, the purification method by the column, etc. had the complicated process, and since it was unsuitable for mass production method, the application to a food raw material was difficult.
[0009] therefore, the shark suitable for the food raw material which the arsenic content of this invention is [a raw material] low, and does not have a different taste and a nasty smell -- it aims at offering a cartilage extract and its manufacture approach.
[0010]
[Means for Solving the Problem] in order to attain the above-mentioned object -- the shark of this invention -- the shark which washed the cartilage extract with water beforehand -- the shark obtained by carrying out demarcation membrane processing of the extract extracted from the cartilage raw material -- it is a cartilage extract and is characterized by an arsenic content being 5 ppm or less.
[0011] this shark -- a cartilage extract -- the conventional shark -- since safety is high since the arsenic content is very low, and there are not a different taste and a nasty smell compared with a cartilage extract, either, it can use for broad food.

[0012] moreover, the shark of this invention -- the manufacture approach of a cartilage extract -- a shark -- the process which washes a cartilage raw material with water, and said shark which washed -- the shark from a cartilage raw material -- the shark obtained at the process which extracts a cartilage extract, and said process -- the shark which was obtained in a cartilage extract at remaining as it is or the process which decolorizes and deodorizes and said process after understanding by the enzyme and which decolorized and deodorized -- it be characterized by to include the process which carries out the demarcation membrane processing of a cartilage extract or its zymolysis liquid.
[0013] according to the above-mentioned invention -- a shark -- most nasty smell components contained in a raw material are easily removable by washing a cartilage raw material with water beforehand. And an arsenic, the different taste, and a nasty smell component are [the extract obtained from the raw material] efficiently removable remaining as it is or by understanding by the enzyme, decolorizing and deodorizing and carrying out demarcation membrane processing further.
[0014] the above-mentioned manufacture approach -- setting -- said washed shark -- the shark from a cartilage raw material -- the extract of a cartilage extract -- said washed shark -- it is desirable to be carried out by adding water to a cartilage raw material and carrying out application-of-pressure heating. According to this mode, the unnecessary protein which is originally insolubility is not eluted, but a mucopolysaccharide can be extracted efficiently.
[0015] moreover, said shark -- decolorization of a cartilage extract or its zymolysis liquid, and deordorization -- said shark -- it is desirable to be carried out by contacting a cartilage extract or its zymolysis liquid to a solid adsorbent. According to this mode, the nasty smell component which was not able to be removed by the coloring and backwashing by water of an extract which were produced at the extract process is removable with sufficient workability.
[0016]
[Embodiment of the Invention] this invention -- setting -- a shark -- a cartilage raw material means the part containing cartilages, such as a fillet of a shark, and kiln. In this invention, it is comparatively easy to receive and the desiccation article of a fillet also with easy handling is used preferably.
[0017] the shark of this invention -- a cartilage extract can be extracted by the following approach.
- backwashing-by-water processing -- a shark -- wash a cartilage raw material with water first. carrying out backwashing by water -- a shark -- although most nasty smell components contained in a cartilage raw material are removed simply, it can do.
[0018] The temperature of wash water has desirable 120 degrees C or less, and is desirable. [of especially 40-100 degrees C] In 120-degree-C **, since the target mucopolysaccharide flows out, the temperature of wash water is not desirable.
[0019] Moreover, although it is also good to pour water, as for the washing approach, it is desirable to carry out by being immersed from the point of efficiency. For example, what is necessary is just to carry out grade immersion for 10 - 120 minutes at the water of extent (usually the amount of one to 5 times of raw material mass) with which a raw material is immersed thoroughly. Moreover, although especially a limit does not have a count of washing, about 1 - 3 times is usually desirable. In addition, washing effectiveness can be gathered from using the wash water (for example, wash water adjusted to pH 9-11 by the sodium hydroxide) which added alkali, a salt, etc.
[0020] - a shark -- the shark from a cartilage raw material -- the shark of the extract above of a cartilage extract which carried out backwashing by water -- from a cartilage raw material, as an approach of extracting an extract, there is especially no limit and it can adopt a well-known approach. For example, the approach of extracting by lye, the approach using a proteolytic enzyme, the approach of extracting with hot water, etc. are employable.
[0021] ** . When adopting the approach of extracting by lye, as lye to be used, a 0.3 - 1.0 mol/L sodium-hydroxide water solution etc. is mentioned, for example. and a shark -- neutralizing and carrying out solid liquid separation by filtration etc., after adding the lye of an amount one to 5 times to the cartilage raw material 100 mass section and extracting at 30-50 degrees C for 1 to 3 hours -- a shark -- a cartilage extract can be obtained.
[0022] ** . When adopting the approach using a proteolytic enzyme, as a proteolytic enzyme to be used, there is especially no limit and the proteolytic enzyme generally used for food manufacturing can be used. and a shark -- carrying out solid liquid separation by filtration etc., after reacting by the optimal conditions of this enzyme and carrying out deactivation of the enzyme suitably using the enzyme of 0.05 - 1 mass % of a cartilage raw material

-- a shark -- a cartilage extract can be obtained.
[0023] ** . -- a shark when adopting the approach of extracting with hot water -- the filtration after adding and heating the water of the amount of one to 5 times to the cartilage raw material 100 mass section, reaching 100-140 degrees C, holding for 0 minute to 5 hours and extracting etc. -- solid liquid separation -- carrying out -- a shark -- a cartilage extract can be obtained.
[0024] In this invention, the approach of extracting with hot water, especially the approach of carrying out an application-of-pressure heating extract are adopted preferably. According to this approach, while being able to prevent decomposition of a mucopolysaccharide, it can extract comparatively efficiently in a short time. concrete -- a shark -- after adding and heating the water of the amount of one to 5 times to the cartilage raw material 100 mass section and reaching 110-130 degrees C, it is most desirable to hold for 0.5 to 3 hours and to extract.
[0025] - a shark -- the shark obtained by the approach of the zymolysis processing above of a cartilage extract -- as for a cartilage extract, it is desirable to process by the proteolytic enzyme further and to carry out depolymerize of the protein contained in an extract. a shark -- by processing a cartilage extract by the proteolytic enzyme and carrying out depolymerize of the protein, the viscosity of this extract can be lowered and the effectiveness of next decolorization, a deordorization process, and demarcation membrane down stream processing can be gathered. in addition, the approach using the proteolytic enzyme of the above-mentioned ** -- a shark -- when a cartilage extract is prepared, since depolymerize of the protein has already been carried out, it is not necessary to perform this process
[0026] Especially the above-mentioned proteolytic enzyme is not restricted, but the proteolytic enzyme generally used for food manufacturing can be used for it. However, since a peptidase is deficient in the capacity to reduce viscosity, it is not so desirable.
[0027] Moreover, although it can set up suitably about the addition, the reaction temperature, and the processing time of an enzyme, it is desirable to set up so that 100cps or less of viscosity of processing liquid may be preferably set to 50cps or less.
[0028] - the shark obtained by decolorization and the approach of the deordorization processing above -- decolorize a cartilage extract or its zymolysis liquid, and deodorize. As for the approach of decolorization and deordorization, it is desirable to use a solid adsorbent from the point of workability. It can use as the above-mentioned solid adsorbent, combining suitably activated carbon, an alumina, silica gel, the activated clay, etc. for example, a shark -- a cartilage extract or its zymolysis liquid -- the activated carbon of 0.5 - 5 mass % -- in addition, what is necessary is to filter and just to collect liquid parts, after agitating at 50-90 degrees C for 15 minutes to 3 hours
[0029] - Carry out demarcation membrane processing of decolorization of the demarcation membrane processing above, and the liquid which carried out deordorization processing further. the shark which was difficult to remove conventionally by this demarcation membrane processing -- while the arsenic of the cartilage raw material origin is easily removable, different tastes, such as a peptide, and a nasty smell component can be removed almost thoroughly.
[0030] As a demarcation membrane used by this invention, NF film of 10 - 60% of salt rejection is desirable. the salt rejection of a demarcation membrane -- the above -- since loss of a mucopolysaccharide becomes it large that it is out of range, yield falls off or it becomes inadequate removing [of different tastes, such as an arsenic and a peptide, and a nasty smell component], it is not desirable.
[0031] In addition, although the conditions of demarcation membrane processing can be set up suitably, it is desirable to usually dilute processing liquid with water so that it may become below solid content concentration about 15 mass %, and to carry out at pH 4-6 and 60 degrees C or less of solution temperature. moreover -- while adding water suitably in this case -- the amount of one to 10 times of the amount of an extract -- the liquid of an amount is made to penetrate three to 5 times preferably
[0032]
[Example] Hereafter, an example is given and this invention is explained concretely.
[0033] an example -- 1 shark, 5kg of fillet desiccation articles was taken out, after putting into 80-degree C water 15L and being immersed for 30 minutes. Water 15L was added and heated to this, and after reaching 120 degrees C, it held for 2 hours and extracted.
[0034] after cooling and a mesh -- a solid -- removing -- a shark -- 16kg (solid content 12 mass %) of cartilage extracts was obtained.
[0035] this shark -- 20g (Amano enzyme company make, trade name "protease P-3G") of proteolytic enzymes

was added to the cartilage extract, and it was made to react to it at 50 degrees C for 1 hour
[0036] Then, after adding 50g (the Takeda Chemical Industries, Ltd. make, trade name "bamboo call 50WR") of powdered activated carbon in this zymolysis liquid and agitating for 30 minutes at 80 degrees C in it, activated carbon was carried out the ** exception and 15kg (solid content 10 mass %) of solutions was collected.
[0037] Demarcation membrane processing of this solution was carried out using NF film (the NITTO DENKO CORP. make, trade name "NTR-7410S2") of 10% of salt rejection.
[0038] The service condition was performed at a part for inlet-pressure 1MPa and flow rate 7L/, and 30 degrees C of solution temperature, and having added water suitably to the concentration liquid side, and maintaining volume at regularity (about 15L), it processed until the amount of permeate liquid was set to 45L. the obtained concentration liquid -- a conventional method -- spray drying -- carrying out -- a shark -- 1kg (powder) of cartilage extracts was obtained.
[0039] the example of a comparison -- except for having used the fillet desiccation article as it was 1 shark, without performing backwashing by water -- an example -- the same -- carrying out -- a shark -- the cartilage extract (powder) was obtained.
[0040] the ** which sets in the example of comparison 2 example, and does not perform NF membrane process for the solution decolorized and deodorized -- as it is -- spray drying -- carrying out -- a shark -- the cartilage extract (powder) was obtained.
[0041] the shark obtained in each above-mentioned example -- component analysis was performed about the cartilage extract. The result is shown in a table 1. In addition, the quantum of an arsenic was performed by atomic absorption spectrophotometry, and the quantum of chondroitin sulfate was performed with the barium-sulfate weight method.
[0042] Moreover, organic-functions assessment was performed about a smell and the taste by ten persons' panelist. The result is combined and is shown in a table 1. in addition, the inside of a table and O: -- x: with strong (there are a little different tastes) **:smell with weak (there is almost no different taste) O:smell with a dramatically weak (there is no different taste) smell -- dramatically -- a smell -- being strong (there being a different taste considerably) -- it expresses.
[0043]
[A table 1]

	質量%	実施例1	比較例1	比較例2
成分分析	水分	4．8	5．1	4．2
	コンドロイチン硫酸ナトリウム	46．8	44．6	33．6
	粗蛋白質	50．4	51．2	56．4
	ヒ素（ppm）	1．9	2．8	46．7
官能評価	臭い	◎	△	×
	味	◎	○	×

[0044] the shark beforehand washed with water from a table 1 -- the shark extracted from the cartilage raw material -- the shark of the example which carried out demarcation membrane processing of the cartilage extract -- the shark of the example 2 of a comparison to which the cartilage extract did not carry out demarcation membrane processing -- compared with a cartilage extract, an arsenic content is dramatically low and it turns out that there are few smells and it is tasty.
[0045] moreover, the shark of the example 1 of a comparison which used the raw material, without washing with water -- although the arsenic content of a cartilage extract is low, it turns out that a smell and the taste are inferior compared with an example.
[0046]
[Effect of the Invention] according to [as explained above] this invention -- a shark -- by washing a cartilage raw material with water beforehand, most nasty smell components contained in a raw material can be removed easily, and an arsenic, the different taste, and a nasty smell component can be efficiently removed for the extract obtained from the raw material remaining as it is or by understanding by the enzyme, decolorizing and deodorizing and carrying out demarcation membrane processing further. consequently, the shark which whose arsenic content is low and does not have a different taste and a nasty smell -- a cartilage extract can be offered.

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TECHNICAL FIELD

[Field of the Invention] the shark which this invention has few arsenic contents, and does not have a different taste and a nasty smell -- it is related with a cartilage extract and its manufacture approach.

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PRIOR ART

[Description of the Prior Art] a shark -- the cartilage extract is widely used as a health food raw material, and the major component is sodium chondroitin sulfate which is about several 100,000 polysaccharide from molecular weight 100,000. Since chondroitin sulfate is widely distributed also over the body and that on the cartilage and the skin of the joint section is especially contained in it, it is used for the health food aiming at an improvement and cosmetics of the osteoarthritis. [many]
[0003] the shark marketed now -- a sodium-chondroitin-sulfate content is 10 - 40%, and the cartilage extract is properly used with the purpose of use and price. Moreover, although the sodium chondroitin sulfate (about 85% or more) which raised whenever [purification] is used as a drugs raw material, it is expensive and it is hard to use it in the food field.
[0004] the former and a shark -- a cartilage extract -- sharks, such as a fillet of a shark, -- after contacting the extract obtained from the cartilage raw material by the approach of carrying out decomposition clearance of the protein which is extracted with lye or neutral salt liquid, and which adds a proteolytic enzyme and lives together etc. to a solid adsorbent and decolorizing and deodorizing, it is manufactured by carrying out spray drying etc.

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EFFECT OF THE INVENTION

[Effect of the Invention] according to [as explained above] this invention — a shark — by washing a cartilage raw material with water beforehand, most nasty smell components contained in a raw material can be removed easily, and an arsenic, the different taste, and a nasty smell component can be efficiently removed for the extract obtained from the raw material remaining as it is or by understanding by the enzyme, decolorizing and deodorizing and carrying out demarcation membrane processing further. consequently, the shark which whose arsenic content is low and does not have a different taste and a nasty smell — a cartilage extract can be offered.

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TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] however, a shark -- many arsenics are contained in the cartilage raw material compared with other raw materials, such as a cow and a cartilage of a salmon, it will be condensed in an extract and a purification process (the conventional shark arsenic content of a cartilage extract : 40-50 ppm), and worth of goods was reduced remarkably.
[0006] furthermore, a shark -- the characteristic low-grade amine etc. existed in the cartilage raw material, just the deordorization processing by the above solid adsorbents of clearance of this nasty smell component is inadequate, and the nasty smell remained in the final product.
[0007] Moreover, clearance of the peptide which presents the bitterness generated with a proteolytic enzyme is difficult for the above-mentioned enzymatic process, and it had had the adverse effect on quality.
[0008] The approach of settling a mucopolysaccharide with alcohol and on the other hand, collecting, the purification method by the column, etc. had the complicated process, and since it was unsuitable for mass production method, the application to a food raw material was difficult.
[0009] therefore, the shark suitable for the food raw material which the arsenic content of this invention is [a raw material] low, and does not have a different taste and a nasty smell -- it aims at offering a cartilage extract and its manufacture approach.

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MEANS

[Means for Solving the Problem] in order to attain the above-mentioned object -- the shark of this invention -- the shark which washed the cartilage extract with water beforehand -- the shark obtained by carrying out demarcation membrane processing of the extract extracted from the cartilage raw material -- it is a cartilage extract and is characterized by an arsenic content being 5 ppm or less.
[0011] this shark -- a cartilage extract -- the conventional shark -- since safety is high since the arsenic content is very low, and there are not a different taste and a nasty smell compared with a cartilage extract, either, it can use for broad food.
[0012] moreover, the shark of this invention -- the manufacture approach of a cartilage extract -- a shark -- the process which washes a cartilage raw material with water, and said shark which washed -- the shark from a cartilage raw material -- the shark obtained at the process which extracts a cartilage extract, and said process -- the shark which was obtained in a cartilage extract at remaining as it is or the process which decolorizes and deodorizes and said process after understanding by the enzyme and which decolorized and deodorized -- it be characterized by to include the process which carries out the demarcation membrane processing of a cartilage extract or its zymolysis liquid.
[0013] according to the above-mentioned invention -- a shark -- most nasty smell components contained in a raw material are easily removable by washing a cartilage raw material with water beforehand. And an arsenic, the different taste, and a nasty smell component are [the extract obtained from the raw material] efficiently removable remaining as it is or by understanding by the enzyme, decolorizing and deodorizing and carrying out demarcation membrane processing further.
[0014] the above-mentioned manufacture approach -- setting -- said washed shark -- the shark from a cartilage raw material -- the extract of a cartilage extract -- said washed shark -- it is desirable to be carried out by adding water to a cartilage raw material and carrying out application-of-pressure heating. According to this mode, the unnecessary protein which is originally insolubility is not eluted, but a mucopolysaccharide can be extracted efficiently.
[0015] moreover, said shark -- decolorization of a cartilage extract or its zymolysis liquid, and deordorization -- said shark -- it is desirable to be carried out by contacting a cartilage extract or its zymolysis liquid to a solid adsorbent. According to this mode, the nasty smell component which was not able to be removed by the coloring and backwashing by water of an extract which were produced at the extract process is removable with sufficient workability.
[0016]
[Embodiment of the Invention] this invention -- setting -- a shark -- a cartilage raw material means the part containing cartilages, such as a fillet of a shark, and kiln. In this invention, it is comparatively easy to receive and the desiccation article of a fillet also with easy handling is used preferably.
[0017] the shark of this invention -- a cartilage extract can be extracted by the following approach.
- backwashing-by-water processing -- a shark -- wash a cartilage raw material with water first. carrying out backwashing by water -- a shark -- although most nasty smell components contained in a cartilage raw material are removed simply, it can do.
[0018] The temperature of wash water has desirable 120 degrees C or less, and is desirable. [of especially 40-100 degrees C] In 120-degree-C **, since the target mucopolysaccharide flows out, the temperature of wash water is not desirable.
[0019] Moreover, although it is also good to pour water, as for the washing approach, it is desirable to carry out by being immersed from the point of efficiency. For example, what is necessary is just to carry out grade

immersion for 10 - 120 minutes at the water of extent (usually the amount of one to 5 times of raw material mass) with which a raw material is immersed thoroughly. Moreover, although especially a limit does not have a count of washing, about 1 - 3 times is usually desirable. In addition, washing effectiveness can be gathered from using the wash water (for example, wash water adjusted to pH 9-11 by the sodium hydroxide) which added alkali, a salt, etc.

[0020] - a shark -- the shark from a cartilage raw material -- the shark of the extract above of a cartilage extract which carried out backwashing by water -- from a cartilage raw material, as an approach of extracting an extract, there is especially no limit and it can adopt a well-known approach. For example, the approach of extracting by lye, the approach using a proteolytic enzyme, the approach of extracting with hot water, etc. are employable.

[0021] ** . When adopting the approach of extracting by lye, as lye to be used, a 0.3 - 1.0 mol/L sodium-hydroxide water solution etc. is mentioned, for example. and a shark -- neutralizing and carrying out solid liquid separation by filtration etc., after adding the lye of an amount one to 5 times to the cartilage raw material 100 mass section and extracting at 30-50 degrees C for 1 to 3 hours -- a shark -- a cartilage extract can be obtained.

[0022] ** . When adopting the approach using a proteolytic enzyme, as a proteolytic enzyme to be used, there is especially no limit and the proteolytic enzyme generally used for food manufacturing can be used. and a shark -- carrying out solid liquid separation by filtration etc., after reacting by the optimal conditions of this enzyme and carrying out deactivation of the enzyme suitably using the enzyme of 0.05 - 1 mass % of a cartilage raw material -- a shark -- a cartilage extract can be obtained.

[0023] ** . -- a shark when adopting the approach of extracting with hot water -- the filtration after adding and heating the water of the amount of one to 5 times to the cartilage raw material 100 mass section, reaching 100-140 degrees C, holding for 0 minute to 5 hours and extracting etc. -- solid liquid separation -- carrying out -- a shark -- a cartilage extract can be obtained.

[0024] In this invention, the approach of extracting with hot water, especially the approach of carrying out an application-of-pressure heating extract are adopted preferably. According to this approach, while being able to prevent decomposition of a mucopolysaccharide, it can extract comparatively efficiently in a short time. concrete -- a shark -- after adding and heating the water of the amount of one to 5 times to the cartilage raw material 100 mass section and reaching 110-130 degrees C, it is most desirable to hold for 0.5 to 3 hours and to extract.

[0025] - a shark -- the shark obtained by the approach of the zymolysis processing above of a cartilage extract -- as for a cartilage extract, it is desirable to process by the proteolytic enzyme further and to carry out depolymerize of the protein contained in an extract. a shark -- by processing a cartilage extract by the proteolytic enzyme and carrying out depolymerize of the protein, the viscosity of this extract can be lowered and the effectiveness of next decolorization, a deordorization process, and demarcation membrane down stream processing can be gathered. in addition, the approach using the proteolytic enzyme of the above-mentioned ** -- a shark -- when a cartilage extract is prepared, since depolymerize of the protein has already been carried out, it is not necessary to perform this process

[0026] Especially the above-mentioned proteolytic enzyme is not restricted, but the proteolytic enzyme generally used for food manufacturing can be used for it. However, since a peptidase is deficient in the capacity to reduce viscosity, it is not so desirable.

[0027] Moreover, although it can set up suitably about the addition, the reaction temperature, and the processing time of an enzyme, it is desirable to set up so that 100cps or less of viscosity of processing liquid may be preferably set to 50cps or less.

[0028] - the shark obtained by decolorization and the approach of the deordorization processing above -- decolorize a cartilage extract or its zymolysis liquid, and deodorize. As for the approach of decolorization and deordorization, it is desirable to use a solid adsorbent from the point of workability. It can use as the above-mentioned solid adsorbent, combining suitably activated carbon, an alumina, silica gel, the activated clay, etc. for example, a shark -- a cartilage extract or its zymolysis liquid -- the activated carbon of 0.5 - 5 mass % -- in addition, what is necessary is to filter and just to collect liquid parts, after agitating at 50-90 degrees C for 15 minutes to 3 hours

[0029] - Carry out demarcation membrane processing of decolorization of the demarcation membrane processing above, and the liquid which carried out deordorization processing further. the shark which was difficult to remove conventionally by this demarcation membrane processing -- while the arsenic of the cartilage

raw material origin is easily removable, different tastes, such as a peptide, and a nasty smell component can be removed almost thoroughly.

[0030] As a demarcation membrane used by this invention, NF film of 10 - 60% of salt rejection is desirable. the salt rejection of a demarcation membrane -- the above -- since loss of a mucopolysaccharide becomes it large that it is out of range, yield falls off or it becomes inadequate removing [of different tastes, such as an arsenic and a peptide, and a nasty smell component], it is not desirable.

[0031] In addition, although the conditions of demarcation membrane processing can be set up suitably, it is desirable to usually dilute processing liquid with water so that it may become below solid content concentration about 15 mass %, and to carry out at pH 4-6 and 60 degrees C or less of solution temperature. moreover -- while adding water suitably in this case -- the amount of one to 10 times of the amount of an extract -- the liquid of an amount is made to penetrate three to 5 times preferably

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EXAMPLE

[Example] Hereafter, an example is given and this invention is explained concretely.
[0033] an example -- 1 shark, 5kg of fillet desiccation articles was taken out, after putting into 80-degree C water 15L and being immersed for 30 minutes. Water 15L was added and heated to this, and after reaching 120 degrees C, it held for 2 hours and extracted.
[0034] after cooling and a mesh -- a solid -- removing -- a shark -- 16kg (solid content 12 mass %) of cartilage extracts was obtained.
[0035] this shark -- 20g (Amano enzyme company make, trade name "protease P-3G") of proteolytic enzymes was added to the cartilage extract, and it was made to react to it at 50 degrees C for 1 hour
[0036] Then, after adding 50g (the Takeda Chemical Industries, Ltd. make, trade name "bamboo call 50WR") of powdered activated carbon in this zymolysis liquid and agitating for 30 minutes at 80 degrees C in it, activated carbon was carried out the ** exception and 15kg (solid content 10 mass %) of solutions was collected.
[0037] Demarcation membrane processing of this solution was carried out using NF film (the NITTO DENKO CORP. make, trade name "NTR-7410S2") of 10% of salt rejection.
[0038] The service condition was performed at a part for inlet-pressure 1MPa and flow rate 7L/, and 30 degrees C of solution temperature, and having added water suitably to the concentration liquid side, and maintaining volume at regularity (about 15L), it processed until the amount of permeate liquid was set to 45L. the obtained concentration liquid -- a conventional method -- spray drying -- carrying out -- a shark -- 1kg (powder) of cartilage extracts was obtained.
[0039] the example of a comparison -- except for having used the fillet desiccation article as it was 1 shark, without performing backwashing by water -- an example -- the same -- carrying out -- a shark -- the cartilage extract (powder) was obtained.
[0040] the ** which sets in the example of comparison 2 example, and does not perform NF membrane process for the solution decolorized and deodorized -- as it is -- spray drying -- carrying out -- a shark -- the cartilage extract (powder) was obtained.
[0041] the shark obtained in each above-mentioned example -- component analysis was performed about the cartilage extract. The result is shown in a table 1. In addition, the quantum of an arsenic was performed by atomic absorption spectrophotometry, and the quantum of chondroitin sulfate was performed with the barium-sulfate weight method.
[0042] Moreover, organic-functions assessment was performed about a smell and the taste by ten persons' panelist. The result is combined and is shown in a table 1. in addition, the inside of a table and O: -- x: with strong (there are a little different tastes) **:smell with weak (there is almost no different taste) O:smell with a dramatically weak (there is no different taste) smell -- dramatically -- a smell -- being strong (there being a different taste considerably) -- it expresses.
[0043]
[A table 1]

	質量%	実施例1	比較例1	比較例2
成分分析	水分	4．8	5．1	4．2
	コンドロイチン硫酸ナトリウム	46．8	44．6	33．6
	粗蛋白質	50．4	51．2	56．4
	ヒ素（ppm）	1．9	2．8	46．7
官能評価	臭い	◎	△	×
	味	◎	○	×

[0044] the shark beforehand washed with water from a table 1 -- the shark extracted from the cartilage raw material -- the shark of the example which carried out demarcation membrane processing of the cartilage extract -- the shark of the example 2 of a comparison to which the cartilage extract did not carry out demarcation membrane processing -- compared with a cartilage extract, an arsenic content is dramatically low and it turns out that there are few smells and it is tasty.
[0045] moreover, the shark of the example 1 of a comparison which used the raw material, without washing with water -- although the arsenic content of a cartilage extract is low, it turns out that a smell and the taste are inferior compared with an example.
[0046]

[Translation done.]

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(54)【発明の名称】　サメ軟骨抽出物及びその製造方法

(57)【要約】
【課題】　ヒ素含量が低く、かつ異味、異臭のない、食品素材に適したサメ軟骨抽出物及びその製造方法を提供する。
【解決手段】　予め水で洗浄したサメ軟骨原料からサメ軟骨抽出液を抽出し、得られたサメ軟骨抽出液をそのまま又は酵素分解した後、脱色、脱臭し、この脱色、脱臭したサメ軟骨抽出液又はその酵素分解液を分離膜処理して、ヒ素含量が低く、かつ異味、異臭のないサメ軟骨抽出物を得る。

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【特許請求の範囲】

【請求項１】　予め水で洗浄したサメ軟骨原料から抽出された抽出液を分離膜処理して得られるサメ軟骨抽出物であって、ヒ素含量が５ｐｐｍ以下であることを特徴とするサメ軟骨抽出物。

【請求項２】　サメ軟骨原料を水で洗浄する工程、前記洗浄したサメ軟骨原料からサメ軟骨抽出液を抽出する工程、前記工程で得られたサメ軟骨抽出液をそのまま又は酵素分解した後、脱色、脱臭する工程、前記工程で得られた脱色、脱臭したサメ軟骨抽出液又はその酵素分解液を分離膜処理する工程とを含むことを特徴とするサメ軟骨抽出物の製造方法。

【請求項３】　前記洗浄したサメ軟骨原料からのサメ軟骨抽出液の抽出は、前記洗浄したサメ軟骨原料に水を加えて加圧加熱することにより行なわれる、請求項２に記載のサメ軟骨抽出物の製造方法。

【請求項４】　前記サメ軟骨抽出液又はその酵素分解液の脱色、脱臭は、前記サメ軟骨抽出液又はその酵素分解液を固体吸着剤に接触させて行なわれる、請求項２又は３に記載のサメ軟骨抽出物の製造方法。

【発明の詳細な説明】

【０００１】

【発明の属する技術分野】本発明は、ヒ素含量が少なく、かつ異味、異臭のないサメ軟骨抽出物及びその製造方法に関する。

【０００２】

【従来の技術】サメ軟骨抽出物は、健康食品素材として広く利用されており、その主要成分は分子量１０万から数１０万程度の多糖類であるコンドロイチン硫酸ナトリウムである。コンドロイチン硫酸は、人体にも広く分布しており、特に、関節部の軟骨や皮膚に多く含まれることから、変形性関節症の改善や美容を目的とした健康食品に利用されている。

【０００３】現在市販されているサメ軟骨抽出物は、コンドロイチン硫酸ナトリウム含量が１０～４０％のものであり、その使用目的及び価格により使い分けられている。また、精製度を高めた（約８５％以上）コンドロイチン硫酸ナトリウムは、医薬品原料として使用されているが、高価であり食品分野では利用しにくい。

【０００４】従来、サメ軟骨抽出物は、サメのヒレなどのサメ軟骨原料から、アルカリ液又は中性塩液で抽出する、蛋白質分解酵素を加えて共存する蛋白質を分解除去する方法等により得られた抽出液を、固形吸着剤に接触させて脱色、脱臭した後、噴霧乾燥等して製造されている。

【０００５】

【発明が解決しようとする課題】しかし、サメ軟骨原料には、ウシやサケの軟骨などの他の原料に比べて多くのヒ素が含まれており、抽出、精製過程で濃縮されてしまい（従来のサメ軟骨抽出物のヒ素含量：４０～５０ｐｐｍ）、商品の価値を著しく低下させてしまっていた。

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【０００６】さらに、サメ軟骨原料には特有の低級アミン等が存在しており、上記のような固形吸着剤による脱臭処理のみでは、この異臭成分の除去が不十分であり、最終製品に異臭が残っていた。

【０００７】また、上記酵素法は、蛋白質分解酵素により生成する苦味を呈するペプチドの除去が困難であり、品質に悪影響を及ぼしていた。

【０００８】一方、アルコールによりムコ多糖類を沈澱させて回収する方法や、カラムによる精製法等は、工程が煩雑で大量生産には不向きであるため、食品素材への応用は困難であった。

【０００９】従って、本発明は、ヒ素含量が低く、かつ異味、異臭のない、食品素材に適したサメ軟骨抽出物及びその製造方法を提供することを目的とする。

【００１０】

【課題を解決するための手段】上記目的を達成するため、本発明のサメ軟骨抽出物は、予め水で洗浄したサメ軟骨原料から抽出された抽出液を分離膜処理して得られるサメ軟骨抽出物であって、ヒ素含量が５ｐｐｍ以下であることを特徴とする。

【００１１】このサメ軟骨抽出物は、従来のサメ軟骨抽出物に比べてヒ素含量が非常に低いため、安全性が高く、また異味、異臭もないので幅広い食品に利用することができる。

【００１２】また、本発明のサメ軟骨抽出物の製造方法は、サメ軟骨原料を水で洗浄する工程、前記洗浄したサメ軟骨原料からサメ軟骨抽出液を抽出する工程、前記工程で得られたサメ軟骨抽出液をそのまま又は酵素分解した後、脱色、脱臭する工程、前記工程で得られた脱色、脱臭したサメ軟骨抽出液又はその酵素分解液を分離膜処理する工程とを含むことを特徴とする。

【００１３】上記発明によれば、サメ軟骨原料を予め水で洗浄することにより、原料に含まれる異臭成分の大部分を簡単に除去できる。そして、その原料から得られた抽出液をそのまま又は酵素分解して、脱色、脱臭し、さらに分離膜処理することにより、効率よくヒ素、異味及び異臭成分を除去することができる。

【００１４】上記の製造方法においては、前記洗浄したサメ軟骨原料からのサメ軟骨抽出液の抽出は、前記洗浄したサメ軟骨原料に水を加えて加圧加熱することにより行なわれることが好ましい。この態様によれば、本来不溶性である不要なタンパク質が溶出せず、効率よくムコ多糖類を抽出できる。

【００１５】また、前記サメ軟骨抽出液又はその酵素分解液の脱色、脱臭は、前記サメ軟骨抽出液又はその酵素分解液を固体吸着剤に接触させて行なわれることが好ましい。この態様によれば、抽出工程で生じた抽出液の着色及び水洗浄で除去できなかった異臭成分を作業性よく除去できる。

【００１６】
【発明の実施形態】本発明においてサメ軟骨原料とは、サメのヒレ、カマ等の軟骨を含む部分をいう。本発明においては、比較的入手しやすく、取り扱いも容易であるヒレの乾燥品が好ましく用いられる。
【００１７】本発明のサメ軟骨抽出物は、下記の方法により抽出することができる。
・水洗浄処理
サメ軟骨原料を、まず水で洗浄する。水洗浄することにより、サメ軟骨原料に含まれる異臭成分の大部分を簡単に除去するができる。
【００１８】洗浄水の温度は１２０℃以下が好ましく、４０～１００℃が特に好ましい。洗浄水の温度が１２０℃超では目的のムコ多糖類が流出してしまうため好ましくない。
【００１９】また、洗浄方法は、水をかけるだけでもよいが、効率性の点から浸漬して行なうことが好ましい。例えば、原料が完全に浸る程度（通常、原料質量の１～５倍量）の水に、１０～１２０分間程度浸漬すればよい。また、洗浄回数は特に制限はないが、通常１～３回程度が好ましい。なお、アルカリや塩などを添加した洗浄水（例えば、水酸化ナトリウムでｐＨ９～１１に調整した洗浄水）を用いることより、洗浄効率を上げることができる。
【００２０】・サメ軟骨原料からのサメ軟骨抽出液の抽出
上記の水洗浄したサメ軟骨原料から、抽出液を抽出する方法としては、特に制限はなく、公知の方法を採用することができる。例えば、アルカリ液で抽出する方法、蛋白質分解酵素を用いる方法、熱水で抽出する方法などを採用することができる。
【００２１】①．アルカリ液で抽出する方法を採用する場合、使用するアルカリ液としては、例えば０．３～１．０ｍｏｌ／Ｌ水酸化ナトリウム水溶液等が挙げられる。そして、例えば、サメ軟骨原料１００質量部に対して１～５倍量のアルカリ液を加え、３０～５０℃で１～３時間抽出した後、中和し、濾過等により固液分離することにより、サメ軟骨抽出液を得ることができる。
【００２２】②．蛋白質分解酵素を用いる方法を採用する場合、使用する蛋白質分解酵素としては、特に制限はなく、一般に食品製造に用いられる蛋白質加水分解酵素を用いることができる。そして、例えば、サメ軟骨原料の０．０５～１質量%の酵素を用いて、該酵素の至適条件で反応を行ない、適宜酵素を失活させた後、濾過等により固液分離することにより、サメ軟骨抽出液を得ることができる。
【００２３】③．熱水で抽出する方法を採用する場合、例えば、サメ軟骨原料１００質量部に対して１～５倍量の水を加えて加熱し、１００～１４０℃に到達してから０分～５時間保持して抽出した後、濾過等により固液分離して、サメ軟骨抽出液を得ることができる。
【００２４】本発明においては、熱水で抽出する方法、特に加圧加熱抽出する方法が好ましく採用される。この方法によれば、ムコ多糖類の分解を防止できると共に、比較的短時間で効率よく抽出することができる。具体的には、サメ軟骨原料１００質量部に対して１～５倍量の水を加えて加熱し、１１０～１３０℃に到達してから０．５～３時間保持して抽出することが最も好ましい。
【００２５】・サメ軟骨抽出液の酵素分解処理
上記の方法で得られたサメ軟骨抽出液は、さらに蛋白質加水分解酵素で処理して、抽出液に含まれる蛋白質を低分子化することが好ましい。サメ軟骨抽出液を蛋白質加水分解酵素で処理して蛋白質を低分子化することにより、該抽出液の粘度を下げることができ、後の脱色、脱臭工程、及び分離膜処理工程の効率を上げることができる。なお、上記②の蛋白質分解酵素を用いた方法でサメ軟骨抽出液を調製した場合は、すでに蛋白質が低分子化されているため本工程を行なう必要はない。
【００２６】上記蛋白質加水分解酵素は、特に制限されず、一般に食品製造に用いられる蛋白質加水分解酵素を用いることができる。ただし、ペプチダーゼは、粘度を低下させる能力に乏しいためあまり好ましくない。
【００２７】また、酵素の添加量、反応温度及び処理時間については、適宜設定できるが、処理液の粘度が１００ｃｐｓ以下、好ましくは５０ｃｐｓ以下になるように設定することが好ましい。
【００２８】・脱色、脱臭処理
上記の方法で得られたサメ軟骨抽出液又はその酵素分解液を、脱色、脱臭する。脱色、脱臭の方法は、作業性の点から固体吸着剤を用いることが好ましい。上記固体吸着剤としては、活性炭、アルミナ、シリカゲル、活性白土などを適宜組み合わせて用いることができる。例えば、サメ軟骨抽出液又はその酵素分解液に、０．５～５質量%の活性炭を加えて、５０～９０℃で１５分～３時間撹拌した後、濾過して液部を回収すればよい。
【００２９】・分離膜処理
上記の脱色、脱臭処理した液を、さらに分離膜処理する。この分離膜処理により、従来除去することが困難であったサメ軟骨原料由来のヒ素を簡単に除去することができると共に、ペプチド等の異味、異臭成分をほとんど完全に除去することができる。
【００３０】本発明で用いられる分離膜としては、食塩阻止率１０～６０%のＮＦ膜が好ましい。分離膜の食塩阻止率が上記範囲外であると、ムコ多糖類の損失が大きくなり収量が落ちたり、ヒ素及びペプチド等の異味、異臭成分の除去が不十分となるため好ましくない。
【００３１】なお、分離膜処理の条件は適宜設定できるが、通常、処理液を固形分濃度約１５質量%以下になるように水で希釈し、ｐＨ４～６、液温６０℃以下で行うことが好ましい。また、この際に、適宜加水しながら、

抽出液の量の１～１０倍量、好ましくは３～５倍量の液を透過させる。

【００３２】

【実施例】以下、実施例を挙げて本発明を具体的に説明する。

【００３３】実施例１

サメヒレ乾燥品５ｋｇを、８０℃の水１５Ｌに入れて３０分間浸漬した後、取出した。これに水１５Ｌを加えて加熱し、１２０℃に到達してから２時間保持して抽出した。

【００３４】冷却後、メッシュで固形物を除去して、サメ軟骨抽出液（固形分１２質量％）１６ｋｇを得た。

【００３５】このサメ軟骨抽出液に、蛋白質加水分解酵素（アマノエンザイム社製、商品名「プロテアーゼＰ－３Ｇ」）２０ｇを添加して５０℃で１時間反応させた。

【００３６】続いて、この酵素分解液に、粉末活性炭（武田薬品工業社製、商品名「タケコール５０ＷＲ」）５０ｇを添加して８０℃で３０分間撹拌した後、活性炭を濾別して、溶液（固形分１０質量％）１５ｋｇを回収した。

【００３７】この溶液を、食塩阻止率１０％のＮＦ膜（日東電工社製、商品名「ＮＴＲ－７４１０Ｓ２」）を用いて分離膜処理した。

【００３８】運転条件は、入口圧力１ＭＰａ、流量７Ｌ＊／分、液温３０℃で行ない、濃縮液側に適宜加水して液量を一定（約１５Ｌ）に保ちつつ、透過液量が４５Ｌになるまで処理を行なった。得られた濃縮液を常法により噴霧乾燥して、サメ軟骨抽出物（粉末）１ｋｇを得た。

【００３９】比較例１

サメヒレ乾燥品を水洗浄を行なわずにそのまま用いた以外は、実施例と同様にして、サメ軟骨抽出物（粉末）を得た。

【００４０】比較例２

実施例において、脱色、脱臭した溶液をＮＦ膜処理を行わずに、そのまま噴霧乾燥してサメ軟骨抽出物（粉末）を得た。

【００４１】上記各例で得られたサメ軟骨抽出物について成分分析を行なった。その結果を表１に示す。なお、ヒ素の定量は原子吸光光度法により行ない、コンドロイチン硫酸の定量は硫酸バリウム重量法により行なった。

【００４２】また、１０名のパネラーにより臭い及び味について、官能評価を行なった。その結果を併せて表１に示す。なお、表中、◎：非常に臭いが弱い（全く異味が無い）、○：臭いが弱い（ほとんど異味が無い）、△：臭いが強い（少し異味がある）、×：非常に臭いが強い（かなり異味がある）、を表す。

【００４３】

【表１】

	質量%	実施例１	比較例１	比較例２
成分分析	水分	４．８	５．１	４．２
	コンドロイチン硫酸ナトリウム	４６．８	４４．６	３３．６
	粗蛋白質	５０．４	５１．２	５６．４
	ヒ素（ｐｐｍ）	１．９	２．８	４６．７
官能評価	臭い	◎	△	×
	味	◎	○	×

【００４４】表１から、予め水で洗浄したサメ軟骨原料から抽出したサメ軟骨抽出液を分離膜処理した実施例のサメ軟骨抽出物は、分離膜処理を行なわなかった比較例２のサメ軟骨抽出物に比べてヒ素含量が非常に低く、また臭いが少なく、味もよいことが分かる。

【００４５】また、原料を水で洗浄せずに用いた比較例１のサメ軟骨抽出物は、ヒ素含量は低いものの、実施例に比べると臭いや味が劣ることが分かる。

【００４６】

【発明の効果】以上説明したように、本発明によれば、サメ軟骨原料を予め水で洗浄することにより、原料に含まれる異臭成分の大部分を簡単に除去でき、その原料から得られた抽出液をそのまま又は酵素分解して、脱色、脱臭し、さらに分離膜処理することにより、効率よくヒ素、異味及び異臭成分を除去することができる。その結果、ヒ素含量が低く、かつ異味、異臭のないサメ軟骨抽出物を提供することができる。